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Colossal Magnetoresistance in La-Y-Ca-Mn-O Films

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Abstract—Magnetoresistance behavior of $La_{0.60}Y_{0.07}CaMnO_x$ thin films epitaxially grown on $LaAlO_3$ has been investigated. The films exhibit colossal magnetoresistance with the MR ratio in excess of 10^8% at ~60K, H = 7T, which is the highest ever reported for thin film manganites. The partial substitution of La^{3+} ions with much smaller Y^{3+} ions results in more than an order of magnitude improvement in MR as compared to the undoped La-Ca-Mn-O material, both in bulk and thin film form. The La-Y-Ca-Mn-O films exhibit a strong dependence of magneto-resistance on film thickness with the maximum MR occurring at a film thickness of ~1000Å.

1. INTRODUCTION

Magnetoresistance behavior of perovskite-like lanthanum manganites such as La-Ca-Mn-O and Pr-Sr-Ca-Mn-O has received much attention in recent years because of the colossal magnetoresistance (CMR) with many orders of magnitude change in resistivity [1]-[5]. In the La-Ca-Mn-O system, e.g., $La_{0.67}Ca_{0.33}MnO_3$, the colossal magnetoresistance generally occurs only in thin films epitaxially grown on substrates with a smaller lattice parameter, e.g., (100) $LaAlO_3$. The bulk $La_{0.67}Ca_{0.33}MnO_3$ material exhibits magnetoresistance ratio $\Delta R/R_H$ of less than ~1000%, 3-4 orders of magnitude smaller than the epitaxial thin films. However, if La (with ionic radius of ~1.22Å) is partially substituted with a smaller rare earth, Y (with ionic radius of ~1.06Å), as in $La_{0.60}Y_{0.07}CaMnO_3$, colossal magneto-resistance now appears in the bulk material with the MR ratio of 10,000% [5]. This is attributed to the change in lattice dimensions such as the Mn-O-Mn bond distance and angle, which are known to affect the metal-insulator and the magnetic transition temperatures.

In this paper, the colossal magneto-resistance behavior of epitaxially grown $La_{0.60}Y_{0.07}CaMnO_x$ films (MR > 10^8%) is described and compared with that of the Y-free, La-Ca-Mn-O films.

2. EXPERIMENTAL PROCEDURES

A dense target, with a nominal composition of $La_{0.60}Y_{0.07}Ca_{0.33}MnO_x$, was prepared by the mixing of high-purity component oxides or carbonates and grinding and sintering at ~1400°C in an O_2 atmosphere. Highly oriented, ~400–2000Å thick La-Y-Ca-Mn-O films were then deposited on (100) $LaAlO_3$ substrates by pulsed laser deposition (PLD). The substrate temperature was maintained at ~700°C during the deposition, which was carried out under a 100 mtorr O_2 partial pressure. The films were post-annealed in 3 atmospheres of oxygen gas at ~850°C.

The resistance and magnetoresistance of the films were measured between 10 and 300 K by the four-point technique and two-point method with a Keithley electrometer in a superconducting magnet with the maximum applied field of 6-8 T. A constant dc current ranging from 1nA to 10μA was used in the four-point technique. The MR value was always negative and isotropic in this study.

3. RESULTS AND DISCUSSION

The as-deposited La-Y-Ca-Mn-O film, ~1000Å thick, exhibits a low MR ratio of only 370% at 85 K and H = 6T. Subsequent heat treatment at 850°C for 2 hours in a 3 atmosphere oxygen dramatically improves the MR ratio to ~2.3×10^7% (H = 6T) and ~10^8% (H = 8T) at 70 K. Shown in Fig. 1 is the resistivity vs

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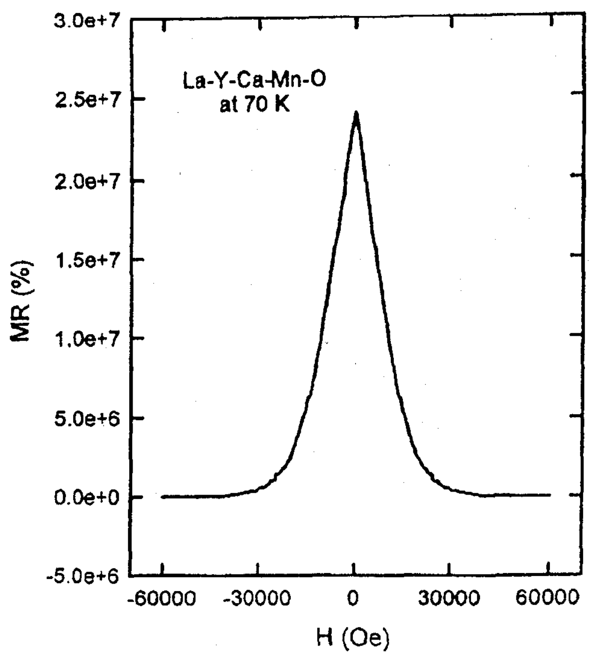

Fig. 1. Resistivity vs field curve for the La-Y-Mn-O film at 70 K (H_{max} = 6T).

H field curve for the La-Y-Ca-Mn-O film at 70K. The zero field resistivity of $\rho = \sim 19300\ \Omega-$cm (resistance $R = 1450\ M\Omega$) is reduced to $\rho = \sim 82\ m\Omega-$cm ($R = 6.12\ k\Omega$) when the in-plane applied field is increased to 6 T. The higher MR ratio of La-Y-Ca-Mn-O film than that of La-Ca-Mn-O film ($\sim 10^6$% at 110K and H = 6T) is most likely related to the Y-doping effect on the lattice parameter/lattice strain.

The change in lattice parameter affects the interatomic distance and bond angle, thus influencing the magnetic exchange interactions between two magnetic cations. As listed in Table 1, the Y-doping of La-Ca-Mn-O compound decreases the lattice parameter

Table 1. MR values (at H = 6T, T = 70-140K) and lattice parameters for La-Ca-Mn-O and La-Y-Ca-Mn-O.

	LCMO	LYCMO
Cation Radius	$r(La^{3+}) = 1.22$	$r(Y^{3+}) = 1.06$Å
Lattice Parameter	a = 3.867	a = 3.859Å
MR(Bulk Materials)	500%	10^4%
MR(Epitaxial Films)	10^6%	23×10^6%

a from 3.867 A to 3.859 A, due to the smaller cation radius of Y^{3+} of 1.06 A as compared to that of La^{3+} (1.22A). Thus, the effect of lattice parameter decrease by Y-doping is superimposed on the similar effect of epitaxy on a smaller lattice substrate ($LaAlO_3$ in this case), and results in a further improvement in colossal magnetoresistance in the La-Y-Ca-Mn-O film. As a result, the CMR effect is much higher in the La-Y-Ca-Mn-O films than in the La-Ca-Mn-O films. It is also interesting to note from Table I that both in bulk materials and epitaxial films, the MR ratio of La-Y-Ca-Mn-O system is roughly ~20 times higher than that of La-Ca-Mn-O system. This result indicates that the lattice engineering seems to be a key to obtaining a large CMR effect.

Shown in Fig. 2 are the temperature dependences of the zero-field resistance R(H = 0) and the high-field resistance R(H = 6T) of the La-Y-Ca-Mn-O film annealed at 850°C for 2 hours. The R(H = 0) is found to monotonically increase as the temperature is lowered. Below 60 K, the resistance at zero magnetic field becomes very high, with R greater than $10^{11}\,\Omega$ exceeding our measurement capability. The resistance at H = 6T also shows an increasing tendency as the temperature is lowered, but reaches a maximum at ~100K and then decreases again.

The temperature dependence of MR ratio in the La-Y-Ca-Mn-O film is shown in Fig. 3. The MR ratio, with a maximum field of 7 T, is just about 500% at 130 K, which progressively increases to $\sim 10^8$%at 60 K.

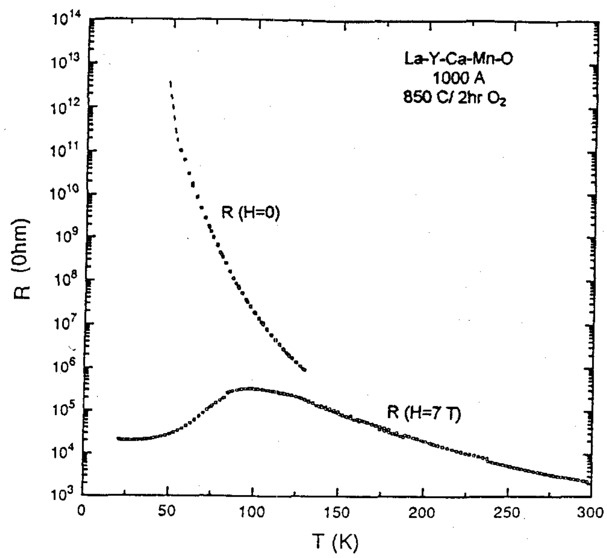

Fig. 2. Temperature dependence of resistance for the La-Y-Ca-Mn-O film at H = 0 and H = 7T, respectively.

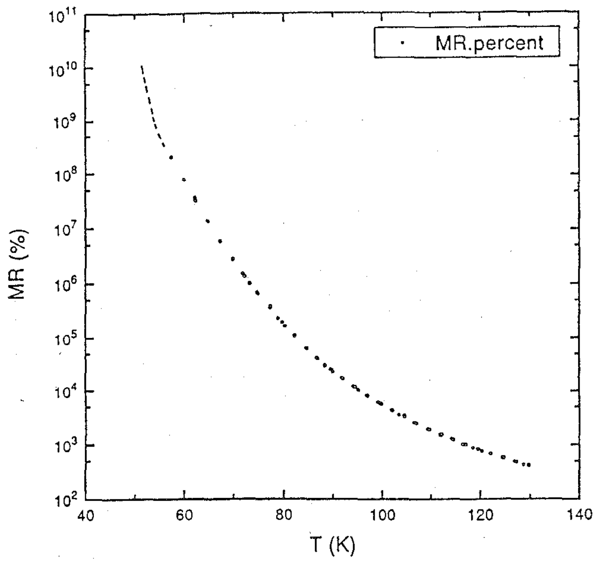

Fig. 3. MR value vs temperature curve for the La-Y-Ca-Mn-O film.

Below 60 K, due to the measurement limit of the electrometer used, the magnetoresistance could not be accurately measured. However, considering the trend in R and MR vs T curves in Figs. 2 and 3, it is more likely that the magnetoresistance ratio of the La-Y-Ca-Mn-O films is at least a few orders of magnitude higher than 10^8%. These MR values in excess of 10^8% are the highest ever reported in the La-Ca-Mn-O system.

It has been found that the CMR value of the La-Y-Ca-Mn-O films exhibit a strong dependence on the film thickness. The maximum MR ratio for a 400Å thick film (800°C/2h heat treated) was $\sim 2 \times 10^6$%, that for a 1000Å thick film was $\sim 2.3 \times 10^7$%, and that for a film with ~2000Å thickness was $\sim 8 \times 10^4$%. Similarly as in the case of La-Ca-Mn-O films [3], the observed thickness dependence of MR in the La-Y-Ca-Mn-O films is tentatively attributed to the change in the lattice strain induced by the change in the thickness of the film deposited on a substrate with a smaller lattice parameter. When the La-Y-Ca-Mn-O film becomes thicker (from 1000Å to 2000Å), the less strained low-resistivity, low-MR region dominates the MR measurement and the MR value decreases. The reason why the La-Y-Ca-Mn-O film much thinner than ~1000Å exhibit reduced MR values even though they are more strained by epitaxy, is still not exactly known at this moment. It may be that there is an optimal lattice strain for the high MR phenomenon. Diffusion-induced contamination of the film from the substrate is another possibility to be considered. When the thickness reduces from 1000Å to 400Å, the electrical resistance drastically increases and causes measurement difficulties. Further research is required to understand the exact mechanisms for the observed thickness dependence behavior.

4. SUMMARY

The CMR behavior in La-Y-Ca-Mn-O epitaxial films has been investigated, and the effects of substrate, temperature and field on MR properties have been discussed. Very large MR values in excess of $\sim 10^8$% is obtained in epitaxially grown La-Y-Ca-Mn-O thin films, which are the highest ever reported for the La-manganite system. A strong thickness dependence of MR behavior has also been observed.

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